Exhibit A

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Mechanical alloying and milling

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Abstract

Mechanical alloying (MA) is a solid-state powder processng technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill. Originally developed to produce oxide-dispersion strengthened (ODS) nickel- and iron-base superalloys for applications in the aerospace industry, MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys. Recent advances in these areas and also on disordering of ordered intermetallics and mechanochemical synthesis of materials have been critically reviewed after discussing the process and process variables involved in MA. The often vexing problem of powder contamination has been analyzed and methods have been suggested to avoid/minimize it. The present understanding of the modeling of the MA process has also been discussed. The present and potential applications of MA are described. Wherever possible, comparisons have been made on the product phases obtained by MA with those of rapid solidification processing, another non-equilibrium processing technique.

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are metastable Zr_2Fe, ω-Zr, and α-Zr, which were not observed during the decomposition of the mechanically alloyed powder [836].

Amorphous phases are synthesized by many other methods also such as laser processing, sputtering, ion mixing, etc. Differences have been observed in the amorphous-phase-forming composition range between MA and these methods. Fig. 34 compares the amorphous-phase-forming composition range for the Ni-Nb system.

There has been lot of activity in recent times on the synthesis/processing and characterization of bulk amorphous alloys [837]. These alloys, characterized by a wide supercooled liquid region (large temperature differences between the crystallization and glass transition temperatures), can be synthesized at extremely low cooling rates. Such alloys have also been synthesized by MA in the multicomponent Zr–Ti–Cu–Ni, Zr–Al–Cu–Ni, and Mg–Y–Cu systems [678]. Applications for such bulk amorphous alloys include the 3 mm-thick faceplate inserts for high-end golf club heads [838].

12. Nanostructured materials

Nanocrystalline materials are single-phase or multi-phase materials, the crystal size of which is of the order of a few (typically 1–100) nanometers in at least one dimension. Because of the extremely small size of the grains, a large fraction of

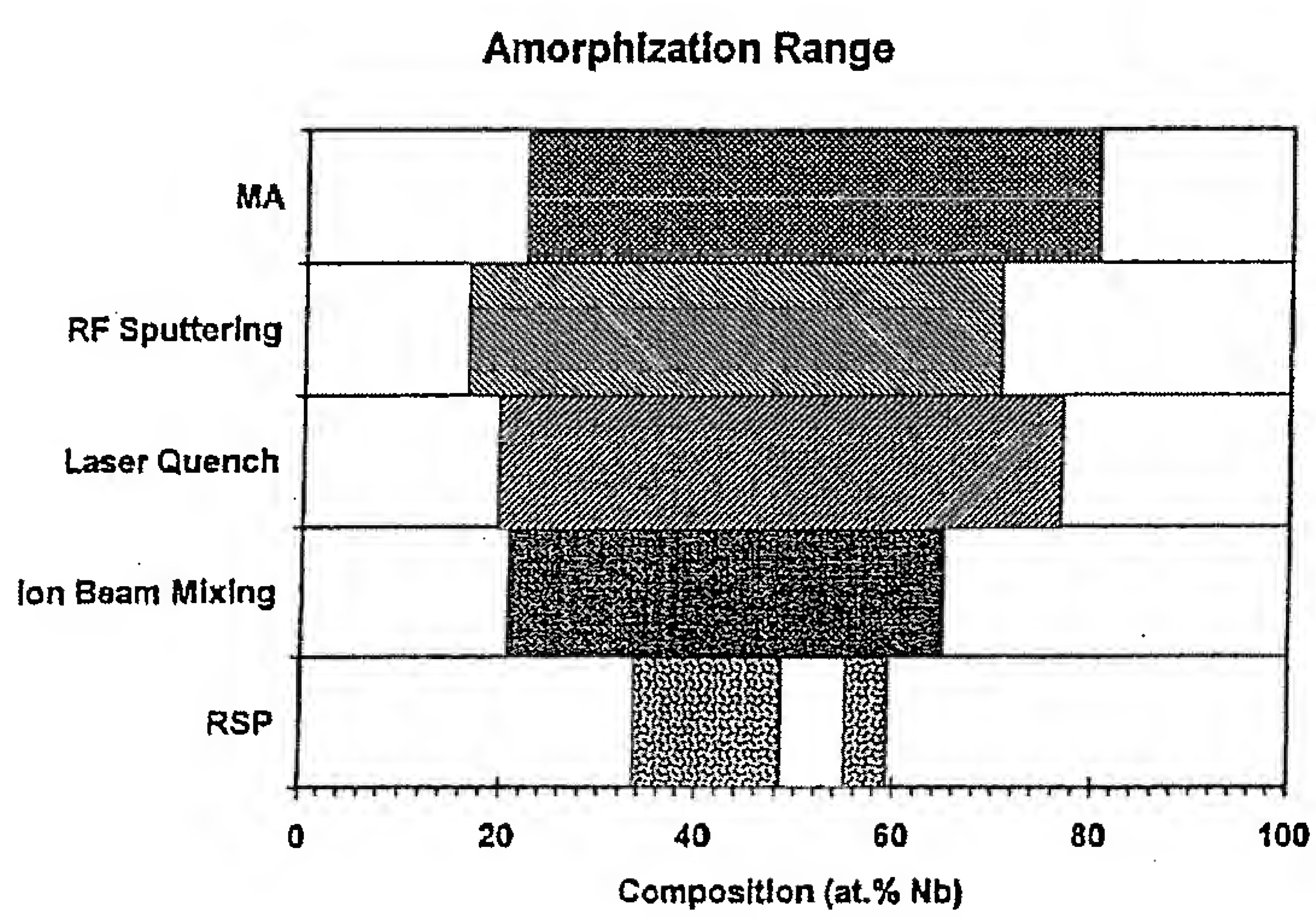

Fig. 34. Comparison of amorphous phase forming range achieved in the Ni–Nb system by different non-equilibrium processing routes.

the atoms in these materials is located in the grain boundaries (Fig. 35) and thus the material exhibits enhanced combinations of physical, mechanical, and magnetic properties (compared to material with a more conventional grain size, i.e., > 1 μm). Nanocrystalline materials show increased strength, high hardness, extremely high diffusion rates, and consequently reduced sintering times for powder compaction. Several excellent reviews are available giving details of the processing, properties, and applications of these materials [183,184,839,840].

Nanocrystalline materials have been synthesized by a number of techniques starting from the vapor phase (e.g., inert gas condensation), liquid phase (e.g., electrodeposition, rapid solidification), and solid state (e.g., mechanical attrition). The advantage of using MA for the synthesis of nanocrystalline materials lies in its ability to produce bulk quantities of material in the solid state using simple equipment and at room temperature. The first report of formation of a nanostructured material synthesized by MA is by Thompson and Politis in 1987 [782], even though the specific mention of formation of "nanometer order crystalline structures produced by mechanical alloying" was by Shingu et al. in 1988 [841]. Koch [183] has summarized the results on the synthesis and structure of nanocrystalline structures produced by mechanical attrition and has recently updated the situation [842].

Grain sizes with nanometer dimensions have been observed in almost all mechanically alloyed pure metals, intermetallics, and alloys (if they continue to be crystalline). Thus, it appears to be a ubiquitous phenomenon. In spite of this, there have not been many investigations to explain why and how the nanometer-sized grains are obtained in these materials. Hellstern et al. [843] have described the mechanism of formation of nanostructures by MA/MM. From high-resolution

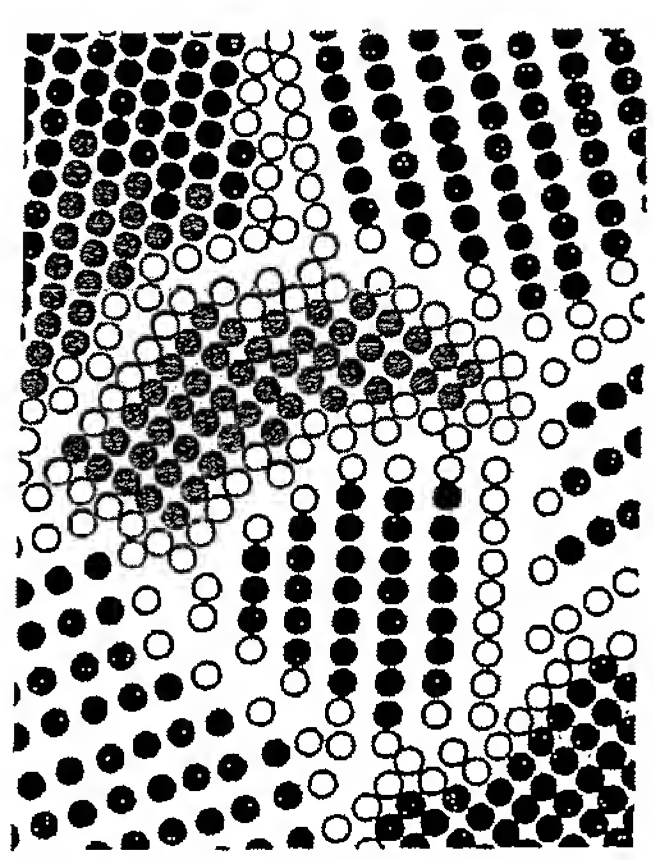

Fig. 35. Schematic arrangement of atoms in an equiaxed nanocrystalline metal.